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GLASSES WITH LEAD SULFIDE NANOPARTICLES FOR LASER TECHNOLOGIES

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The formation of nanoparticles of semiconducting lead sulfide in silicate and borosilicate glasses matrices is investigated. The dependence of the size of PbS particles on the temperature-time heat-treatment conditions is identified. The effect of clarification arising in these nanostructural glass materials is established. The glasses developed can be used as solid passive locks in lasers radiating in the short IR spectrum range.

The contemporary phase of science of materials, solid bodies technologies, and physics of solid bodies and semiconductors is closely related to the synthesis of quantum-scale structure and studies of various quantum-scale effects inherent in such structures. Quantum-scale objects are solid structures in which electron excitations are limited in one, two, or three dimensions. Of special interest are nanosized (quasizero-dimensional) structures, as these systems have extremely small “nanoscopic” sizes, not more than a few nanometers in all three dimensions [1]. These nanostructures can be formed in different dielectric matrices: glass, polymer, etc. However, the optimum basis for their formation is inorganic glass of different chemical compositions: silicate, borate, borosilicate, germanate, etc. The main advantages of these matrices include high optical quality of glass, and high thermal conductivity and radiation resistance.

The research and development of nano-scale structures makes it possible to synthesize new optical materials for quantum electronics, optoelectronics, and laser engineering.

Glasses containing nanoscale particles (nanoparticles) of semiconductive lead sulfide PbS are attracting special interest both in the theoretical and practical aspects. On the one hand, PbS nanoparticles constitute a model object for studying effects manifested in semiconductors under the condition of a severe restriction of charge carriers motion in three dimensions. On the other hand, glasses containing PbS nanoparticles are promising as passive locks in lasers emitting in the short IR spectrum range, in order to obtain pulses of a millimicrosecond and ultrashort duration. Lead sulfide has a small effective mass of charge carriers (electron and holes), a narrow prohibited zone width E_{gap} , and a large Bohr radius

of the exciton. If the size of the nanoparticle size is close to the Bohr radius of the exciton, a quantum-scale effect arises, which is manifested in the shift of the fundamental absorption edge of the semiconductor toward shorter wavelengths and the emerging of clearly defined absorption bands related to exciton resonances. The absorption saturation (decrease) in the range of these resonances (primarily of the first one, with the lowest energy, indicated in Fig. 1 as $|j_c = 1/2, \pi_c = -1\rangle \rightarrow j_v = 1/2, \pi_v = 1\rangle$ in accordance with the accepted terminology [2]) under an intense light effect is used in passive laser locks for the formation of radiation pulses of millimicrosecond and ultrashort duration [3, 4].

By controlling the size of PbS nanoparticles it is possible to shift the position of the absorption peak caused by the first exciton resonance (to modify the energy of the first exciton resonance) in a wide spectral range and thus to shift the operating wavelength of the passive lock by using only one semiconductive material, namely, PbS. A passive lock made

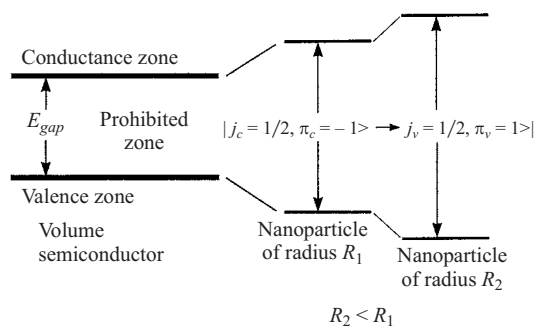


Fig. 1. Scheme of energy structure of volume semiconductor and semiconductor nanoparticles of different sizes.

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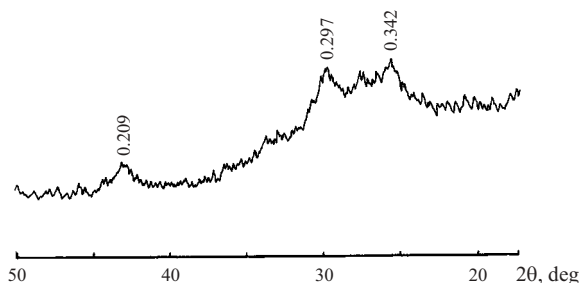


Fig. 2. Diffraction pattern of glass containing PbS nanoparticles.

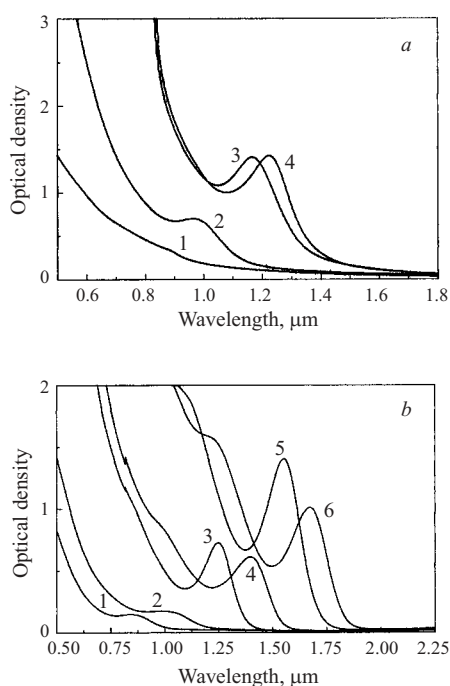


Fig. 3. Optical absorption spectra of silicate (a) and borosilicate (b) glasses with PbS nanoparticles. Curve numbers correspond to sample numbers in Table 1.

of glass with PbS nanoparticles under low intensity of incident light radiation has a high absorption coefficient, i.e., the lock is shut. Under intense resonance excitation, when the light intensity significantly increases, the absorption coefficient perceptibly decreases and the clarification effect is manifested: the lock is open and transmits the laser beam.

Earlier PbS nanoparticles of size 7–30 nm in a matrix based on silicate glass have been produced and analyzed at the Corning Glass company (U.S. patent No. 5449645) [5].

The formation of smaller PbS nanoparticles in a matrix based on phosphate glass has been reported, which made it possible to obtain the absorption peak of the first exciton resonance in the interval around 1.0–1.1 μm [6].

The purpose of our study is to investigate the formation of nanoparticles of semiconductive PbS in silicate and borosilicate glass matrices and to identify effects emerging in these nanostructural glass materials.

Silicate and borosilicate matrix glasses were synthesized at a temperature of $1400 \pm 50^\circ\text{C}$ in a gas flame furnace with a 2 h exposure at the maximum melting temperature. To produce a semiconductor phase in the matrix glass, lead oxide and sulfur were taken as modifiers and added directly into the batch prepared of glass components. The finished glass melt was cast into metallic molds to produce samples for subsequent thermal treatment; the samples were annealed at 450°C .

Based on the results of gradient crystallization, glasses that had a steady vitreous state in the temperature interval of the formation of semiconductor PbS phase were selected for research. The semiconducting PbS nanoparticles were formed in a glass matrix in thermal treatment of glass. The precrystallization period, in which crystallization centers (nuclei) are formed, is important for the heat-treatment stage. In this context, we determined the softening temperature of experimental glasses and, accordingly, selected the thermal treatment regimes for glass matrices. For silicate and borosilicate matrices the formation of nanoparticles was conducted in the temperature interval of $450 - 525^\circ\text{C}$. The exposure duration varied in the limits of 1–25 h.

The results of the experiments demonstrated that at 450°C with a maximum exposure duration the nanoparticles of the semiconductor phase are not formed. The formation of lead silicate nanoparticles starts at a temperature of 480°C and more, which is corroborated by x-ray phase analysis. Figure 2 shows the diffraction pattern of a glass matrix, in which PbS nanoparticles have been formed as a consequence of heat treatment. The main interplanar distances (0.342, 0.297, and 0.209 nm) correspond to the interplanar distances of crystalline PbS (the data of the Joint Committee on Powder Diffraction Standards, 1989).

It should be noted that certain difficulties in growing PbS nanoparticles are involved in obtaining a uniform distribution over the glass matrix volume. In our opinion, the localization of nanoparticles in certain parts of the matrix and their complete absence in other parts occurs due to the microinhomogeneity of the matrix structure, presumably caused by composition or density fluctuations.

A difference in glass exposure duration under thermal treatment affects the growth of the semiconductor phase nanoparticles. Figure 3 shows the optical absorption spectra of silicate and borosilicate glasses subjected to thermal treatment under different temperature-time regimes.

Different heat temperature duration yields nanoparticles of different sizes. In a silicate matrix nanoparticles are virtually not formed under heat treatment at 480°C and exposure for 10 h; there is no peak on the absorption spectrum. Extending the heat treatment duration to 15, 20, and 25 h at the same temperature (480°C) facilitates the formation of nanoparticles of size 3.8, 4.6, and 4.8 nm, respectively, and, accordingly, shifts the first exciton absorption peak to the long-wave spectrum range (0.97, 1.16, and 1.22 μm).

A similar situation is observed in a borosilicate matrix as well. As a consequence of heat treatment PbS nanoparticles of size 3.4, 4.0, 4.9, 5.6, 6.5, and 7.2 nm were grown in the borosilicate matrix. As nanoparticles grow, the optical absorption spectra exhibit a shift of the first exciton absorption peak toward longer waves (0.86, 1.02, 1.25, 1.39, 1.55, and 1.67 μm). A two-stage heat treatment schedule of the borosilicate matrix (the first stage — 480°C, exposure for 24 h and the second stage — 525°C for 5 h) resulted in the growth of the smallest nanoparticles (3.4 nm), which corresponds to the maximum energy of the first resonance: 1.43 eV and the shortest wavelength of the absorption band: 0.86 μm .

The temperature-time conditions of heat treatment of silicate and borosilicate glass, as well as the sizes of PbS nanoparticles formed under these conditions and the spectral positions of the first exciton absorption peak are specified in Table 1. The size of PbS nanoparticles is determined in accordance with [2].

We have established a clarification effect in experimental glasses, i.e., the absorption coefficient of the glass decreases, as the incident radiation intensity grows. The residual absorption in the clarified state is approximately 0.2 of the initial absorption. The absorption coefficient related to the optical inhomogeneity of samples is equal to less than 0.1 cm^{-1} .

Using a passive lock based on silicate glass containing PbS nanoparticles of size 4.6 nm, light pulses of 100 nsec duration were obtained in laser in erbium glass (radiation wavelength 1.54 μm).

Thus, a technology of the formation of lead sulfide nanoparticles in glasses of the silicate and borosilicate systems has been developed and the conditions for the thermal treatment of glasses for the formation of nano-scale PbS particles in the glass matrix have been determined. The dependence of the size of nanoparticles on the temperature-time heat-treatment conditions has been established.

By controlling the heat-treatment regime, it is possible to form semiconductor lead sulfide particles of different sizes in a glass matrix and thus to shift the optical absorption edge within a wide wavelength interval and, accordingly, modify the working wavelength of the passive laser lock using only one semiconducting material, that is, PbS.

The new nanostructural glass materials will find application as clarifying media (solid-body passive locks), which

TABLE 1

Sample	Treatment conditions		Average diameter of nanoparticle, nm	Spectral position of absorption band maximum of the first exciton resistance	
	temperature, °C	duration, h		wavelength, μm	photon energy (resonance energy), eV
Silicate glass					
1	480	10	—	None	—
2	480	15	3.8	0.97	1.28
3	480	20	4.6	1.16	1.07
4	480	25	4.8	1.22	1.02
Borosilicate glass					
1	480	24	3.4	0.86	1.43
	525	5			
2	525	1	4.0	1.02	1.22
3	525	10	4.9	1.25	0.99
4	525	15	5.6	1.39	0.89
5	525	20	6.5	1.55	0.80
6	525	25	7.2	1.67	0.74

can generate short and ultrashort pulses for wavelengths of 0.80 – 1.75 μm in lasers used for medicine, fiberoptic communications, and remote probing of the atmosphere.

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